Characterization of Controlled Flash Pyrolysis Coal Liquids

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Among the currently available coal liquefaction processes, the Controlled Flash Pyrolysis (CFP) process developed by Occidental Research Corporation is unique in several respects. The CFP process uses the hydrogenated recycle solvent for the quenching of pyrolysis vapors. The solvent (in most cases tetralin is used as a model solvent) functions as a diluting factor to decrease the probability of polymerization and as hydrogen-shuttling agent to prevent the reactive free radicals in coal liquid from further reactions. The coal liquid thus obtained is presumably lighter and better in quality.[1] The determinations of the chemical nature and composition of the CFP coal liquids are therefore essential in understanding both the liquid quality and the quenching mechanism of our process.

Coal liquid is a complex mixture; its understanding can be determined by both the study of its general characteristics (statistically average properties), and by a detailed analysis of its chemical composition. Techniques developed for the study of heavy oils from petroleum can be applied for coal liquid samples. In this study for the determination of average property, the conventional methods, such as elemental analysis, solvent classification test, GPC, and ASTM D1160 distillation for the liquid analysis were employed. The recently developed technique of Field Ionization Mass Spectrometry (FIMS) which produces only molecular ions with very little fragmentation has also been utilized for the determination of molecular weight distribution. The detailed analysis of coal liquefaction products is difficult. Due to the complexities of the liquid samples, structural analyses are usually limited to oil and asphaltene fractions.[2,3,4] Chromatographic technique must be used for separation before spectroscopic methods can be applied. M. Farcasiu[5] has employed chromatographic fractionation method analyzing not only asphaltene (benzene-soluble) but also preasphaltene materials. J. E. Dooley has performed an extensive study on the characterization of syncrudes from coal. A GPC-MS correlation was developed in that study.[6] In the present study we have separated coal liquid into fractions according to boiling point, polarity and acidity/basicity. Combined spectroscopic methods are then utilized for its chemical characterization.

Wyodak coal was used for the pyrolysis and the pyrolysis temperature varied from 1100°F to 1600°F unless otherwise specified. The model quench solvent, tetralin with 10% of m-cresol was used for the quenching of coal pyrolysis vapors. The role of m-cresol can be two-fold: 1) increase the solubility of coal liquid in tetralin, 2) promote the hydrogen-shuttling mechanism.[7] The removal of quench solvent which was carried out by Kugelrohr distillation (10μ, 50°C) was necessary before the analysis of coal liquid began. During the process of solvent removal, volatile materials inevitably codistilled. The coal liquid samples discussed here are therefore the 400°F+ material.

Elemental Analysis and Solvent Classification Test

The general characterization of coal liquid starts with elemental analysis and solvent classification test. As shown in Table 1, as the pyrolysis temperature increases, the oil content and aromaticity of the liquid increases accordingly, whereas the oxygen content decreases. A similar finding was reported in the H-NMR study on the influence of pyrolysis temperature on the aromatic fraction and the phenolic content.[8] It was suggested that larger fused aromatic ring systems are produced and additional pyrolytic reactions occurred at higher temperatures.

Table 1

Some Chemical Properties of Coal Liquids Prepared at Different Pyrolysis Temperatures

	Liquid			
	1100°F	1200°F	1300°F	1600°F
C wt %	79.79	81.25	82.14	84.73
H wt %	7.24	6.80	6.21	4.72
N wt %	1.11	1.15	1.17	1.58
S wt %	0.34	0.35	0.42	0.51
O wt %	11.34	10.23	10.05	4.86
H/C	1.09	1.00	0.91	0.69
oil[a]		40.6	46.0	56.3
asphaltene[b]		39.8	21.8	26.0
preasphaltene[c]		19.6	26.6	16.3

[a] material that is pentane soluble
[b] material that is pentane insoluble, but toluene soluble
[c] material that is toluene insoluble, but pyridine soluble

Volatility

The volatility of coal liquid was also studied. Because of the interference of quench solvent, tetralin and m-cresol, the amount of material which boils below 400°F was corrected for their presence as determined by GC.

The 400°F+ material was then subjected to ASTM D1160 distillation. Since the distillation required significant amounts of material, only two samples (1200°F and 1600°F) were studied using this technique. Instead, field ionization mass spectrometry which is useful for molecular weight distribution determination was employed.

FIMS was found to be useful in the measurement of volatility studies. This is achieved since the sample in the probe can only be vaporized in vacuo under proper heating. The change of ion intensities with the change of probe temperature therefore reflects the boiling point range of the mixture, although the ionization potential of the components may slightly influence the precision of this method. This approximation may be tolerable when the volatilities of different coal liquid samples are compared, considering the similarity of multi-component profiles among liquid samples. Fig. 1 shows the comparison of the volatility of samples from different pyrolysis temperatures using the FIMS technique. Temperature 1600°F generates the lightest material.

Thermogravimetric Analysis is currently being investigated for obtaining data on the sample volatility. Preliminary results on creosote oil (Fig. 2) showed excellent correlation among D1160, simulated GC distillation and TGA. Deviations occurred only in the high temperature region. The advantage of this method is that only a minute amount of sample is needed, and the cost of the analysis is low. The major difference between TGA and distillation is that the distillation is carried out in an equilibrium state, whereas TGA is carried out under the flow of an inert gas.

Molecular Weight Distribution

Molecular weight distribution of coal liquids was determined by Gel Permeation Chromatography (GPC) and FIMS. The pyrolysis temperature effect on the molecular weight distribution is illustrated in Fig. 3 and Table 2 as determined by GPC and FIMS respectively.

Table 2

Effect of Pyrolysis Conditions on Coal Liquid 400°F+ (FIMS Study)

Pyrolysis Condition	% Volatilized	Number Ave. M. Wt.	Wt. Ave. M. Wt.
1100°F	89	343	400
1200°F	88	307	344
1300°F	87	275	303
1600°F	88	284	310

The trend of decreasing average molecular weight with increasing pyrolysis temperature is consistent in both studies.

Compositional Analysis

Comparison of FIMS of coal liquids obtained at different pyrolysis temperatures reveals significant differences in their compositions (Fig. 4). We have therefore chosen two samples (1200°F and 1600°F) for comprehensive characterization. The method developed by J. E. Dooley[6] was adapted with some modification in the separation of the liquid mixture. The procedure includes a three-tiered separation: distillation, acid/base extraction and liquid-solid chromatography as shown in Fig. 5. Three distillation cuts (400-650°F, 650-740°F, 740-870°F) from the 1600°F sample and two distillates (400-650°F, 650-700°F) from the 1200°F sample were used for the further separation. Extraction with 1N NaOH and 1N HCl respectively gave the percentages of acids, bases and neutrals as listed in Table 3.

Table 3

Distribution of Acids, Bases and Neutrals
in Coal Liquid Sample

<table>
<tr><th colspan="2">Coal Liquid</th><th>Acid</th><th>Base</th><th>Neutral</th></tr>
<tr><td rowspan="2">1200°F</td><td>distillate 1
(400-650°F)</td><td>31.4%</td><td>4.8%</td><td>63.1%</td></tr>
<tr><td>distillate 2
(650-700°F)</td><td>27.5%</td><td>7.6%</td><td>62.1%</td></tr>
<tr><td rowspan="3">1600°F</td><td>distillate 1
(400-650°F)</td><td>3.2%</td><td>4.5%</td><td>88.5%</td></tr>
<tr><td>distillate 2
(650-740°F)</td><td>2.6%</td><td>3.1%</td><td>91.4%</td></tr>
<tr><td>distilalte 3
(740-870°F)</td><td>4.5%</td><td>1.6%</td><td>73.0%</td></tr>
</table>

The acidic portion present in the 1600°F sample is considerably lower than the 1200°F, which is in agreement with the lower oxygen content discussed before. These polar compounds (acids and bases) are currently being investigated by C-13 NMR and IR to obtain information on the distribution of functional groups containing heteroatoms such as oxygen and nitrogen. The neutral fractions were then further separated into subfractions by chromatographic methods utilizing both silica and alumina in a single column, eluting with hexane, benzene/hexane (5%, then 20%), $CHCl_3$, and finally $CH_3OH/CHCl_3$ (10%). The subfractions collected which presumably are saturates, monoaromatics, diaromatics and polyaromatics were further examined by their retention factors (R_f) on thin layer chromatography against standards (benzene, naphthalene, and phenanthrene). The efficiency of the dual packed column separation are being studied by GC-MS. The results will be discussed.

ACKNOWLEDGMENTS

Partial support from Department of Energy for this project is highly appreciated.

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FIGURE 1

Volatility of Pyrolysis Liquids by FIMS

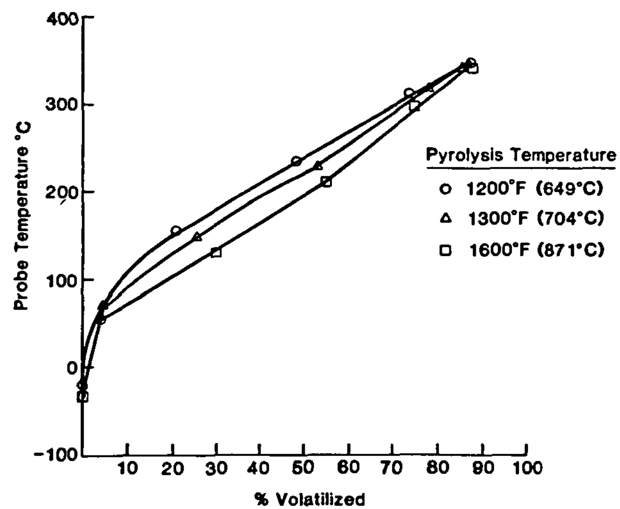


Figure 2
Distillation Curves of Creosote Oil

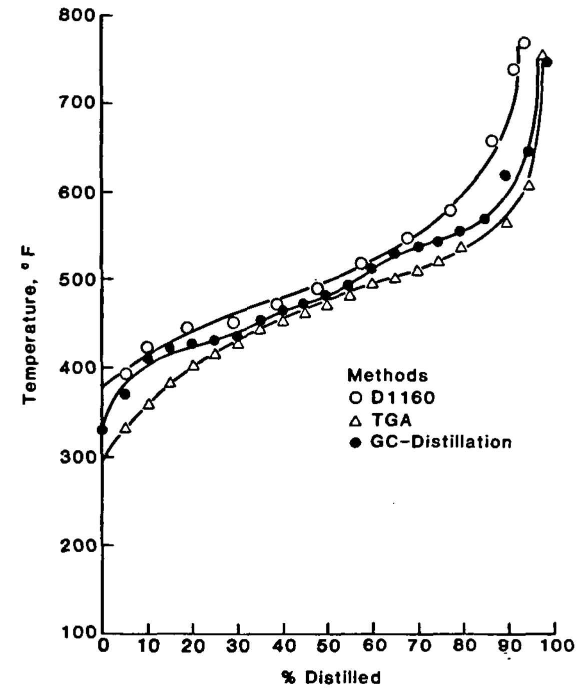


Figure 3

Gel Permeation Chromatograms of Coal Liquids

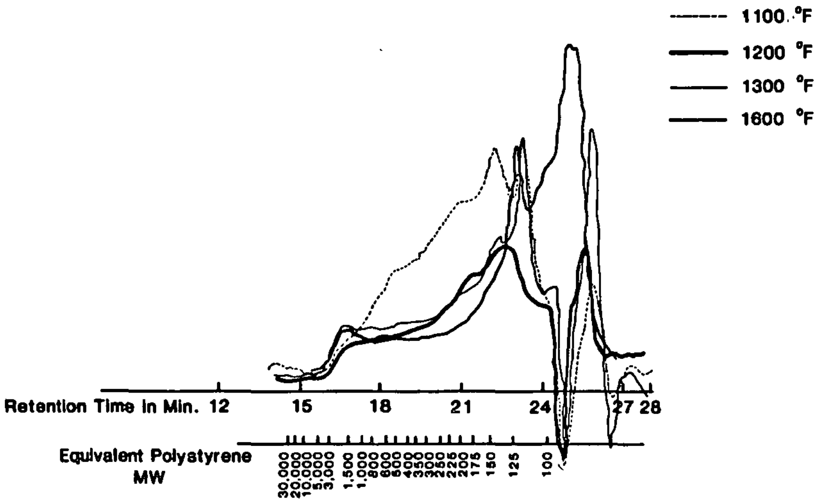


FIGURE 5

Separation and Characterization Procedure for Coal Liquids

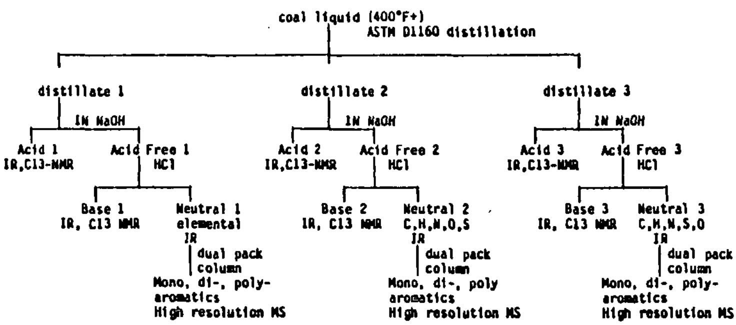
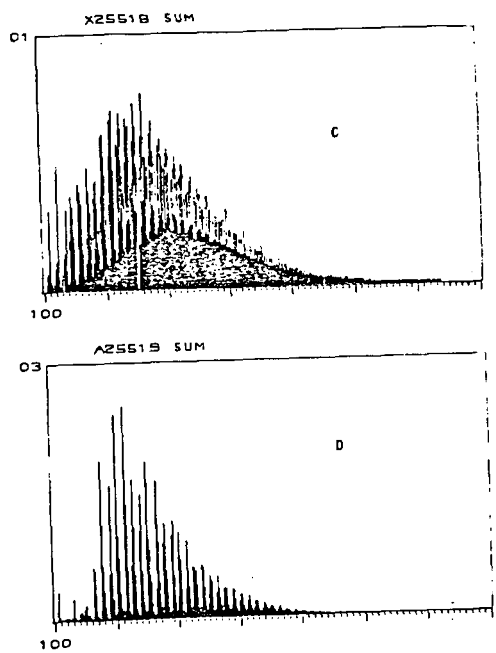


FIGURE 4b

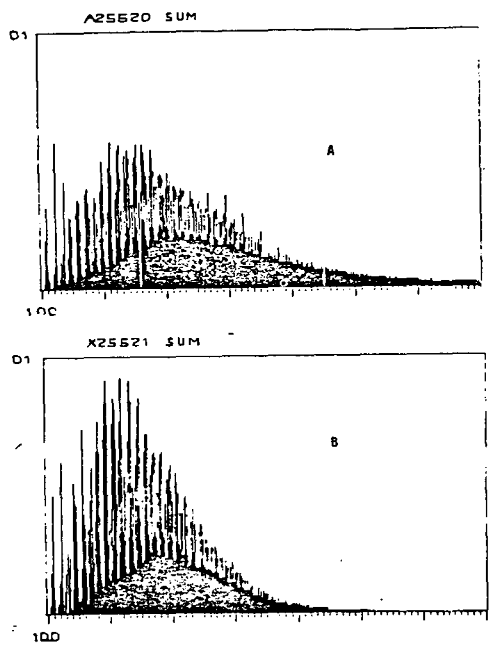
Comparison of FIMS of Coal Liquid Samples
Obtained at Different Temperatures



C: 1200°F
D: 1600°F

FIGURE 4a

Comparison of FIMS of Coal Liquid Samples
Obtained at Different Temperatures



A: 1100°F
B: 1300°F